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(54) ELECTRODE FOR BATTERIES

(71) We, MATSUSHITA ELECTRIC INDUSTRIAL COMPANY LIMITED, a Japanese Company of 1006, Oaza Kadoma, Kadoma-shi Osaka-fu, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to fuel cells, and to electrodes for such cells. More specifically, the invention relates to cells in which the fuel is hydrazine, sodium borohydride or formalin. For the purpose of the present specification, a cell is to be considered as either a single cell or an assembly of single cells.

Compounds such as hydrazine and sodium borohydride are very suitable for use as the fuel for a fuel cell, since polarisation of the fuel electrodes can be maintained at a low level even during relatively high discharge rates of the cell, because of the high activity of these compounds. A cell using a fuel electrode of this material, and used in conjunction with an oxidising electrode for a suitable oxidising agent such as air, can give high discharge current densities, provided that a suitable catalyst is included in the electrodes. Suitable catalysts for the fuel electrode include platinum group catalysts, including platinum itself, whilst suitable catalysts for the oxidising electrode include silver, metal oxides and active carbon; these are relatively inexpensive as compared with the platinum group catalysts.

Fuel electrode catalysts such as platinum, palladium and alloys of platinum with other metals are very satisfactory as catalysts for fuel electrodes, but have the great disadvantage of being very expensive. Even though a very small proportion of the catalyst per unit area of the electrode is required, with practical fuel cells the cost of the catalyst comes high, and sometimes prohibitively high. The cost of the catalyst may have a determining effect on the practical application of the fuel cell, in competition with other current generat-

ing devices, such as solar cells, air-metal batteries and conventional primary and secondary cells.

It is desirable that any form of cell should maintain a steady electromotive force over its working life, and the life should be as extended as possible. In the case of the fuel cell, this requires that the catalyst should remain effective over the prolonged working life.

At one time, the characteristics of a fuel cell were to a large extent determined by the limitations of the oxidising electrode, but of late there have been improvements in this respect. In consequence, there is at the present time an even greater demand for a fuel electrode for a fuel cell which is effective in use and which is of low cost. The present invention is concerned with an improved fuel electrode, and a cell embodying such an electrode.

The invention includes a method of making an electrode for a fuel cell which includes reducing a solution containing a nickel salt and a copper salt and caustic alkali and using the resultant material as a catalyst in an electrode. The invention also includes an electrode when produced by said method.

Features and advantages of the invention will also appear from the following description of embodiments thereof, given by way of example, in conjunction with the accompanying drawings, in which:—

Figure 1 is a diagrammatic vertical sectional view through an air-hydrazine fuel cell;

Figure 2 is a graph showing the relationship between electrode potential and current density for an electrode;

Figure 3 is a graph showing the variation of electrode potential with discharge time of an electrode;

Figure 4 is a diagrammatic vertical sectional view of another form of oxygen-hydrazine fuel cell; and

Figure 5 is a diagram showing the arrange-

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ment of a device for measuring the discharge characteristic of a cell.

We have considered the use of nickel black, nickel boride, iron and mixtures of these compounds with additives as a catalyst for a fuel electrode. These materials are much less expensive than platinum and similar catalysts, but their performance is inferior. It is found that initially nickel and similar catalysts maintain their activity over a period of discharge, so that the voltage is maintained and the polarisation of the electrode will be kept at a low figure. However, with extended use of the electrode it is found that the electrode potential falls and over periods of discharge of some thousands of hours there is an appreciable drop in potential of the electrode. We have found that the voltage drop is caused largely by oxidation of the surface of the metal catalyst, though loss of the catalyst from the surface of the electrode may be a contributory cause. It appears that in use these catalysts are polarised anodically in the presence of a reducing agent such as hydrazine, and it is the thought that this is the reason why the catalysts are slowly oxidised over an extended period. Further, if by neglect or mischance, or by reason of excessive current discharge, there may be caused a degree of oxidation of the electrode such that the electrode cannot recover its initial performance and there is permanent impairment of the electrode potential.

We have found that the performance of a fuel electrode containing nickel black as a catalyst is very substantially improved by the embodiment in the nickel black of copper. So far as we are aware, it has not been appreciated that copper is effective to suppress the oxidation of nickel which normally occurs when the nickel is immersed in a caustic alkali electrolyte in the presence of a reducing substance such as hydrazine. Nickel black is finely divided metallic nickel in the form of a soft dull black powder.

Further, we have found that copper contributes to the formation of nickel black from a nickel salt in the presence of hydrazine. Normally, it is not practicable to make nickel black merely by reacting a nickel salt with hydrazine in a caustic alkali. However, if a copper salt is present, even to a small extent, in the nickel salt in these conditions, copper is first formed from the copper salt by the action of the hydrazine, and the copper thus formed acts as nuclei for the formation of the nickel black from the nickel salt. This action proceeds rapidly; this fact may be indirect evidence of the action of the copper in suppressing oxidation of the nickel black.

We have also discovered that when copper is added to the nickel black as a catalyst, the fuel electrode has good powers of recovery after any shortage of supply of fuel to the cell.

The catalyst consisting of nickel black and

copper can be prepared basically by reduction of a mixed aqueous solution of nickel salt and copper salt. Reduction can be effected by heating the solution in a reducing atmosphere such as hydrogen, by the electro-deposition of the catalyst in the aqueous solution, or by treating the catalyst with hydrazine in alkali. Of these methods, the last is preferred; the two former methods have the disadvantage of the activity and bond strength of the electrode and the catalyst formed, and the complexity of the process.

The methods of producing an electrode embodying the catalyst can be placed broadly in three groups: a first group in which the catalyst alone, but with a binder, is moulded under pressure into the shape of the electrode, a second group in which the catalyst is mixed with a carrier powder and the mixture, together with a binder, is moulded under pressure into the shape of the electrode, and the third group in which a carrier compound is first moulded to form a substrate of the electrode, and the catalyst is then supported on the surface of the substrate.

In the first case, the powdered catalyst can be mixed, for example, with a solution of a polystyrol or a powdered fluorine containing resin, the mixture being moulded under pressure round a reinforcing metal grid or screen. In the second case, the catalyst can be added to, for example, carbon powder, and the electrode produced by moulding round the reinforcement as before. In the third possibility, nickel powder, for example, can be sintered on to the surface of a metal grid or screen, and the catalyst then applied to the surface of the sintered nickel support.

The following are Examples of the second and third methods for the production of the hydrazine fuel electrode of a fuel cell.

EXAMPLE 1.

Nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) were mixed in a proportion such that the ratio of nickel ions to copper ions present is 2 to 1. One part by weight of this mixture was dissolved in water and dissolved to give an aqueous solution of the nitrates. An excess amount of 15% by weight aqueous solution of sodium carbonate was added to the solution of the nitrates, maintaining the solution at 40°C , the mixture being well stirred. The resultant precipitate was separated, and to it added a solution containing 1 mol of caustic potash and 1 mol of hydrazine hydrate (100% by weight solution of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$), the solution being added gradually. Reduction proceeded rapidly, to give a black metal powder. After being thoroughly washed with water, the metal powder was dried at normal temperature under reduced pressure. A mixture was prepared consisting of 2 parts by weight of carbon powder and 0.7 parts by weight of ethy-

lene tetrafluoride-propylene hexafluoride copolymer, with one part by weight of the mixed metal black; a mixing device was used to assure thorough mixing. The mixed powder was placed in a suitable mould, so as to enclose a metal reinforcing grid in the centre of the mould, and the powder moulded to shape using a pressure of 350 kg/cm². After moulding, the electrode had a thickness of 1.1 mm. A small area of the electrode layer was removed to reveal the metal grid, and a terminal connection made to the grid by means of a thin nickel plate, connected to the screen by spot welds.

For the purpose of comparison, a second electrode was prepared, similar to the first, but differing from it in the omission of the copper. It is convenient to identify the copper containing electrode as electrode A and the other as electrode B.

The two electrodes were used in the construction of two similar fuel cells, the construction of which is indicated in Figure 1. The cell comprises a casing 10 of a suitable material such as polyvinyl chloride in one open face of which is located the air electrode 11. The hydrazine electrode 12 is separated from the air electrode by a separator 13 of asbestos. The cell defines a chamber 14 for the fuel, with an inlet port 15 and an outlet port 16. Terminal devices 17 and 18 are provided respectively for the electrodes 11 and 12.

The air electrode 11 may consist of a moulded mixture of active carbon, silver and a water repellent and a suitable fuel consists of an aqueous solution of caustic potash, having a specific gravity of 1.35 and containing 2% by weight of hydrazine hydrate.

Two such cells, one using an electrode of type A and the other of type B, were then subjected to tests to examine the potential of the fuel electrode for different values of current density, and the results are indicated in the graph of Figure 2. The electrode potential is given with reference to a standard mercury oxide electrode, and the current density is measured in milliamperes per square centimetre. The measurements were made at a temperature of 30°C. Figure 2 shows that there is not any substantial difference between the performance of the two cells in this respect.

A further series of tests were made between the two cells, in which the two cells were subjected to continuous discharge at a current corresponding to a current density of 55 mA/cm², the results being shown in a graph of Figure 3. In these tests, the temperature of the cells was kept within the range of 32° to 38°C. Figure 3 shows that over a protracted period of discharge, the performance of the cell with electrode A was better than that of the cell with electrode B. This trend was observed at both higher and lower tem-

peratures of the electrolyte and it was observed also that for currents corresponding to a current density greater than the figure specified, the difference between the potentials of both electrodes became greater.

EXAMPLE 2.

Nickel nitrate and copper nitrate were mixed in a proportion such that the ratio of nickel ions to copper ions was 3 to 1; the mixture was dissolved by adding to it 0.8 parts by weight of water for each part by weight of the mixture, to produce an aqueous solution of the nitrates. A sintered nickel plate, giving 78% porosity and having a thickness of 0.9 mm. was immersed in an aqueous solution of the nitrates at 35°C. for five minutes, in order that the solution could be fully absorbed into the pores of the sintered plate. The plate was then dried for two hours at 95°C. After drying, the plate was immersed in 7 mol aqueous solution of caustic potash at room temperature for five minutes and then in 5 mol aqueous solution of caustic potash containing 3% by weight hydrazine hydrate, at room temperature. After leaving the plate in the solution for 2 to 3 hours, the solution was heated to 45°C. and the plate was then left further in the solution for 1 hour. Under these conditions, nickel black and copper are formed from the nitrates. The plate was then washed and the very small amount of catalyst present on the surface of the sintered plate was removed and the plate dried under reduced pressure. The electrode was then completed in the manner described above. A terminal for the device was connected to a point of the sintered nickel plate by spot welding before the catalyst was applied to it.

Figure 4 is a diagrammatic vertical sectional view through a multiple unit fuel cell, using electrodes produced in the manner described. In Figure 4, the unit cells are indicated at C₁, C₂, . . . etc. The cells are similar in construction, so that one only of the cells will be described. This comprises a housing 20 for the cell; each cell includes two hydrazine electrodes 21, separators 22 and oxygen electrodes 23. The cell is formed to provide a fuel chamber 24, with an inlet 25 leading to a fuel supply conduit 26, and an outlet 27 leading to a conduit 28, the two conduits 26 and 28 being common to the cells of the composite unit. The electrodes are provided with terminals 29 and 30, with the similar electrodes of each cell being connected together by weight. A very suitable fuel consists of an electrolyte formed of a 30% by weight aqueous solution of caustic potash containing 1.8% by weight of hydrazine hydrate.

Ten cells of the type described were connected in voltage-aiding series connection, and were then subjected to a test by means of a test device shown diagrammatically in Figure

5. In this device the assembly of cells 30 is mounted in a container 31, and supported above a container 32, containing electrolyte 33. The fuel containing electrolyte 33 is fed to the cell by pump 34. Nitrogen gas evolved in the reaction of the cells is released to atmosphere through an exhaust port 35 and the fuel in the electrolyte 33 could be replenished from an 80% by weight aqueous solution of hydrazine hydrate in a container 36, admitted to the container 32 at a controlled rate through valve 37. Oxygen gas is supplied from a pressure container, not shown, to an inlet 38, and a small proportion of unused oxygen gas and a small proportion of nitrogen which is released from the electrolyte after passing around the oxygen electrodes, are discharged through a vent pipe 39.

The device of Figure 5 was used to test two cells, each comprising an assembly of single cells, the construction of which was similar, but of which one, which can be identified as cell C, using a catalyst of both nickel black and copper, the other cell having a fuel electrode which included no copper. This latter cell is identified as cell D. The two cells were discharged at a current corresponding to a current density of 70 mA/cm² for 100 hours repeatedly at an interval of 10 hours. After 10 hours of discharge, it was found that there was no substantial difference between the terminal voltages of the cells C and D, cell C having a voltage of 7.7 V and cell D a voltage of 7.5 V. However, as the period of discharge increased, the difference between the two cells progressively increases, cell C becoming more clearly better than cell D. Thus, after a discharge time of 350 hours, the terminal voltage of cell C was 7.8 V, whilst that of cell D was 7.6 V. After 500 hours the corresponding voltages were 7.5 V for cell C and 7.2 V for cell D. After a total of 800 hours, the voltage of cell D had dropped to 6.8 V, whilst cell C was 7.3 V. At 1200 hours, the voltage of cell D was 6.4 V and of cell C 7.1 V. At a total discharge time of 2500 hours, cell D had a voltage of only 5.7 V, whilst the voltage of cell C was still 6.7 V. During the period of discharge, the potential of the oxygen electrodes remained substantially unchanged, and the drop in terminal voltage is due substantially entirely to the potential change of the hydrazine electrodes.

From the two Examples given, it will be seen that a catalyst which consists of nickel black and copper retains its activity over a longer period of time than a catalyst which contains no copper. The addition of the copper to the nickel black appears to be effective down to very small proportions of copper, since the effect of the copper lies in inhibiting the oxidation of the nickel. For example, although in the two Examples given, copper was added to nickel in the proportion of 1 to 2 and 1 to 3, the addition of copper in a

proportion as small as 1 to 10 brings a perceptible effect. The preferred range of copper is one in which the copper is added such that the ratio of copper to nickel ions is in the range of 0.05 to 0.5.

It is to be understood that since the effectiveness of the copper lies in inhibiting the oxidation of the nickel, as described above, additives such as iron, silver, cobalt and tungsten can be used, in addition to the copper.

WHAT WE CLAIM IS:—

1. A method of making an electrode for a fuel cell which includes reducing a solution containing a nickel salt and a copper salt and caustic alkali and using the resultant material as a catalyst in an electrode.
2. A method in accordance with claim 1 wherein said solution is reduced in the presence of hydrazine.
3. A method in accordance with claims 1 or 2, and comprising moulding under pressure a mixture of the catalyst, an alkali resistant electrically conductive powder and a binder.
4. A method in accordance with claim 3 wherein said conductive powder is carbon powder.
5. A method of making an electrode for a fuel cell, which comprises forming a porous electrode substrate, applying thereto a solution containing nickel salt and copper salt and thereafter reducing the solution in the pores of the substrate with caustic alkali and a reducing agent.
6. A method according to claim 5 wherein said reducing agent is hydrazine.
7. A method in accordance with claim 6 in which said porous electrode substrate is a sintered nickel plate.
8. An electrode for a fuel cell, which includes as a catalyst nickel black and copper, when prepared by a method according to any of the preceding claims.
9. An electrode in accordance with claim 8, and including also iron, silver, cobalt or tungsten.
10. An electrode in accordance with claim 8 or 9 comprising a compressed body of material including said catalyst and means for making electrical connection to said body.
11. An electrode in accordance with claim 10, and comprising a reinforcing conductive structure within said body of material.
12. An electrode in accordance with claim 11, wherein said structure is a metallic grid.
13. An electrode in accordance with claims 11 or 12, wherein said electrode includes a base of sintered nickel on which the catalyst is supported.
14. A fuel cell including an electrode in accordance with any of claims 8 to 14.
15. An improved electrode according to claim 8 for a fuel cell, substantially as described with reference to the accompanying drawings.

16. An improved fuel cell according to claim 14 substantially as described with reference to the accompanying drawings.

- 5 17. An improved method of making a fuel cell, according to claim 1, substantially as described with reference to the accompanying drawings.

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